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Surface cleaning and modification of Si(100) substrates by ethanol and water cluster ion beams

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The interactions of ethanol and water cluster ions with Si(100) substrates were investigated. The Si substrates were sputtered by the ethanol cluster ion beams, and the sputtering yield for the cluster ion irradiation at an acceleration voltage of 9 kV was approximately 100 times larger than that for argon monomer ion irradiation at the same acceleration voltage. In addition, surface cleaning of the Si substrates, on which a small amount of metal vapors such as Cu, Al, and Au was deposited previously as contaminative particles, was performed by irradiation of the ethanol cluster ion beams. X-ray photoelectron spectroscopy measurements showed that the contaminative metal particles were removed from the Si surface at an ion dose of 1×10^{15} ions/cm^2. Furthermore, contact angles as well as Fourier transform infrared spectra of the Si surfaces were measured, and the wettability of the surfaces changed drastically depending on the irradiation conditions of the ethanol and water cluster ions. This is ascribed to the difference in the chemical modification of the Si surfaces by the functional groups, which were produced after the impact of the ethanol and water cluster ions on the Si surfaces. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2172342]

I. INTRODUCTION

The demand for material processing technologies for advanced semiconductor devices has recently been increasing, and the development of specific surface processes such as shape-controlled synthesis on the surface[1] and atomic level control during film growth[2] has been required. With the progress to various kinds of electronic, optical, and magnetic devices, control of the fabrication process at an atomic level becomes more important.[3,4] Furthermore, the surface cleaning and modification processes have an important role in the device fabrication, and various kinds of dry processes as well as wet processes are applied to the surface treatment.

The cluster ion beam process is one of the basic technologies in nanostructure fabrications such as deposition, dry etching or cleaning.[5–9] It has several advantages for the surface treatment, one of which is that the high-energy-density deposition and the collective motions of the cluster atoms during impact play important roles in the surface process kinetics.[5,6] Another advantage is that equivalently low-energy and high-current ion beams can be realized using cluster ion beams.[9] However, cluster ion beam processing using liquid source materials has not been fully assessed as the production of such cluster beams is not widely available. With regard to liquid sources, which include organic materials, one of their excellent features is the presence of various kinds of structures and chemical properties permitting chemical modification of the solid surfaces. In addition, the physical and chemical properties of the cluster ions are different from those of bulk state, and the liquid cluster ion beam process is expected to exhibit unique characteristics such as high-rate sputtering and various chemical modifications of solid surfaces at room temperature. We have developed a new type of liquid cluster ion source and applied it to surface cleaning and modification of Si(100) surfaces[10,11] using irradiation by ethanol and water cluster ions. The resulting surface modification has been investigated using x-ray photoelectron spectroscopy (XPS), contact angle measurements, and Fourier transform infrared (FT-IR) spectra.

II. EXPERIMENTAL PROCEDURE

The detail of the experimental apparatus was described elsewhere.[10] Briefly, liquid materials such as ethanol and water were introduced into the cluster source. The liquid materials were heated up to 150 °C, and the vapors of the liquid materials were ejected through a nozzle into a vacuum region such as 10^{-2} Torr. When the vapor pressure was larger than 1000 Torr, the vaporized liquid clusters such as ethanol and water clusters were produced by an adiabatic expansion phenomenon. The cluster size, which was measured by time-of-flight (TOF) method, was distributed between a few hundreds and a few tens of thousands, and the peak size was about 500 to 1000 molecules for the ethanol and about 2500 molecules for the water, respectively. The cluster beams formed were ionized by electron bombardment, and the cluster ion was assumed to be singly charged state. The ionization voltage (V_e) was adjusted between 100 and 500 V, and the electron current for ionization (I_e) was adjusted between 100 and 500 mA. The cluster ions were accelerated toward a substrate, which was set on a substrate holder. The acceleration voltage (V_a) was adjusted between 0 and 10 kV. The substrates used were Si(100), and the substrate temperature was room temperature. To be compared with the Si(100) surfaces, SiO_2 films with a thickness of 500 nm, which were thermally grown on the Si(100) substrates, were also irradi-

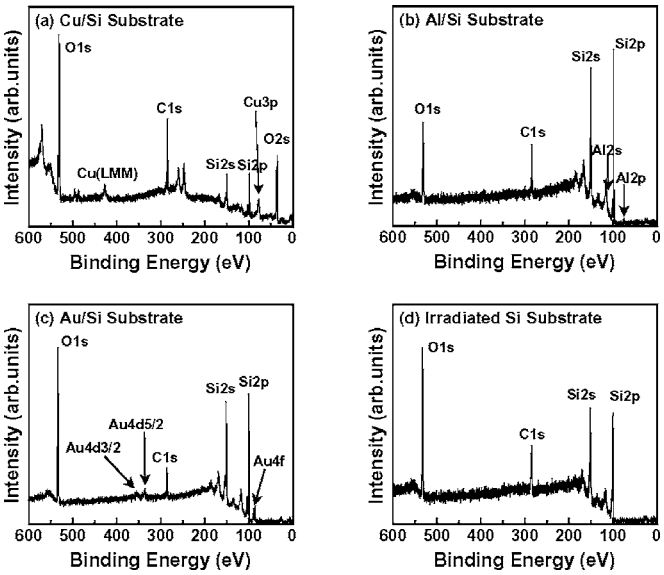

FIG. 1. XPS spectra for Si surfaces contaminated with (a) Cu, (b) Al, and (c) Au particles, and (d) for the Si surface after irradiation of the ethanol cluster ion beams. The ion dose was 1×10^{15} ions/cm^2.

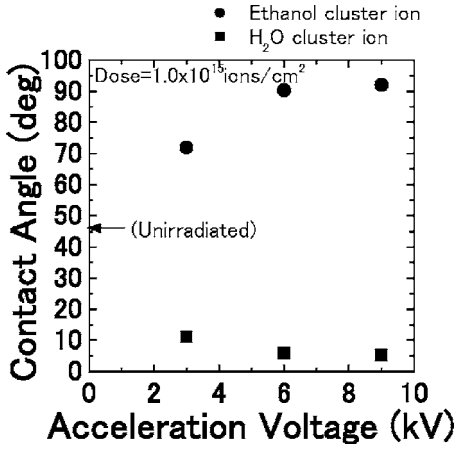

FIG. 2. Dependence of the contact angle on the acceleration voltage for ethanol and water cluster ion irradiations. The ion dose was 1×10^{15} ions/cm^2.

ated by the liquid cluster ion beams. The background pressure around the substrate was 2×10^{-7} Torr, which was attained using a turbo-molecular pump.

The sputtering effect by irradiation of ethanol cluster ions on Si(100) and SiO_2 surfaces at an ion dose of 1.0×10^{15} ions/cm^2 was investigated.[10] The sputtered depth was measured by the step profiler (Veeco Instruments: DEKTAK-3173933). The sputtered depth increased with the increase of the acceleration voltage, and at an acceleration voltage of 9 kV it was 344.6 nm for the Si surface and 47.2 nm for the SiO_2 surface, respectively. The sputter profile at an area of 5×5 mm^2 was very smooth, and the error in the sputter depth was within a few percent. The sputtering yield of the Si surface was 178 atoms per ion, which was approximately 100 times larger than that by argon ion beam sputtering at an acceleration voltage of 9 kV. Furthermore, with regards to the sputtering ratio of Si to SiO_2 for the ethanol cluster ion irradiation, the ratio increased with decreasing acceleration voltage.

III. RESULTS AND DISCUSSION

The surface cleaning of Si(100) substrates, on which metal vapors such as Cu, Al, and Au were deposited previously as contaminative particles, was performed by irradiation of ethanol cluster ion beams. Figure 1 shows the XPS spectra for Si(100) surfaces contaminated with (a) Cu, (b) Al, and (c) Au particles, and (d) for the Si surface after irradiation of the ethanol cluster ion beams, respectively. The cluster size used was larger than 100 molecules per cluster, and the irradiation condition was at an acceleration voltage of 9 kV and an ion dose of 1×10^{15} ions/cm^2. The amount of the contaminative metal particles was about 1×10^{13} atoms/cm^2. For the Si surfaces before irradiation of the cluster ion beams, XPS peaks corresponding to deposited metal particles appear together with C_{1s} and O_{1s} peaks. For all the irradiated surfaces, the metal XPS peaks disappear, and metal particles are removed by the irradiation of the ethanol cluster ion beams. The C_{1s} and O_{1s} peaks were larger than those for the unirradiated Si(100) surfaces. Furthermore, XPS depth profile measurements showed that the C_{1s} and O_{1s} peaks were not present from the Si(100) surface etched to a depth of 0.5 nm. This indicates that organic materials such as ethanol molecules remain on the Si surfaces after irradiation of the ethanol cluster ions, and they are not included in the Si substrates. In addition, an atomic force microscopy (AFM) measurement showed that the surface roughness for the irradiated Si substrates was less than 1 nm for an area of 1×1 μm^2 and the smooth surface at an atomic level was obtained even after sputtering. This is ascribed to the lateral sputtering effect of the cluster ion beams,[6] which is enhanced with increasing acceleration voltages.

The wettability of the Si surfaces irradiated by ethanol and water cluster ion beams was investigated by measuring the contact angles for water droplets, which were placed on top of the Si(100) samples immediately after their removal from the vacuum chamber. The variation of contact angles measured at different places were within a few degrees. Figure 2 shows the dependence of the contact angle on the acceleration voltage for ethanol and water cluster ion irradiation. The ion dose was 1×10^{15} ions/cm^2. The cluster size was larger than 100 molecules per cluster. To be compared with the irradiated Si surface, the contact angle for the unirradiated Si surface was also measured. As shown in the figure, for the case of ethanol cluster ion irradiation, the contact angle increases with increasing acceleration voltage. It is larger than 90° at an acceleration voltage of 9 kV, and the hydrophobic property of the Si surface is enhanced at higher acceleration voltages. On the other hand, for the case of water cluster ion irradiation, the contact angle decreases with increase of the acceleration voltage. It is less than 5° at an acceleration voltage of 9 kV, and the hydrophilic property of the Si surface is enhanced at higher acceleration voltages. For the irradiation of the cluster ions at higher acceleration voltages, the Si substrates are sputtered out, and more dangling bonds induced on the Si surface have a bond with the alkyl or hydroxyl radicals, depending on the irradiation of the ethanol or water cluster ions.

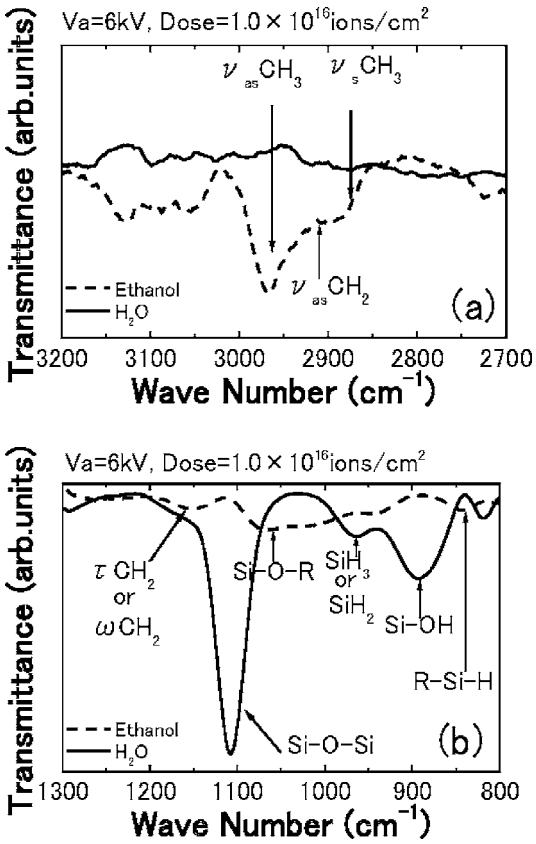

FIG. 3. FT-IR spectra for the Si surfaces irradiated by ethanol and water cluster ions for the wave number of (a) 2700–3200 cm^{-1} and (b) 800–1300 cm^{-1}. The ion dose was 1×10^{16} ions/cm^2.

According to the wettability measurement, the Si surfaces irradiated by ethanol and water cluster ions showed the different chemical modification. In order to clarify the difference in the surface state of the irradiated surface, the optical transmittance was measured by using FT-IR spectroscopy (Nicolet: MAGNA-IR 860). Figure 3 shows the transmittance of the Si surfaces irradiated by the ethanol and water cluster ions for the wave number of (a) 2700–3200 cm^{-1} and (b) 800–1300 cm^{-1}, respectively. The ion dose was 1×10^{16} ions/cm^2, and the peaks were smaller at lower ion doses. For the ethanol cluster ion irradiation, the vibration peaks about 3000 cm^{-1} appear. The peaks correspond to the CH_3 and CH_2, which are not observed in the spectra for the water cluster ion irradiation. On the other hand, in the spectra between 800 and 1300 cm^{-1}, the vibration peaks such as Si–O–Si, Si–OH, SiH_3, etc., appear for the water cluster ion irradiation. These peaks are not observed in the spectra for the ethanol cluster ion irradiation. Based on the wettability measurement for the irradiated surfaces, the Si surface atoms have a bond with the alkyl radicals after ethanol cluster ion irradiation and the hydroxyl radicals after the water cluster ion irradiation, respectively.

The surface cleaning of Si(100) substrates, on which metal vapors such as Cu, Al, and Au were deposited previously as contaminative particles, was performed by irradiation of ethanol cluster ion beams. XPS measurement showed that the contaminative metal particles were removed from the Si surfaces at an ion dose of 1×10^{15} ions/cm^2. Furthermore, the wettability of the Si(100) surfaces irradiated by ethanol and water cluster ion beams were investigated by measuring the contact angles for water droplet. The contact angle increased with the increase of acceleration voltage for the ethanol cluster ion irradiation, and it was larger than 90° at an acceleration voltage of 9 kV. The hydrophobic property of the Si(100) surface was thus enhanced by the irradiation of the ethanol cluster ions. On the other hand, for the water cluster ion irradiation, the contact angle decreased with the increase of acceleration voltage, and it was less than 5° at an acceleration voltage of 9 kV. The wettability of the Si surface was much enhanced by the irradiation of the water cluster ions. In addition, the FT-IR measurement showed that the dangling bonds induced on the Si surfaces had a bond with the alkyl groups such as CH_3 for the ethanol cluster ion irradiation and with the hydroxyl groups for the water cluster ion irradiation, respectively. Thus, the liquid cluster ion beams have unique characteristics suitable for surface treatment such as surface cleaning and chemical modification, which are not achieved by the conventional wet process.

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